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(6) SORPTION AND TRANSPORT OF WATER VAPOR
IN GLASSY POLYACRYLONITRILE.

by

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SORPTION AND TRANSPORT OF WATER VAPOR IN GLASSY POLYACRYLONITRILE

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ABSTRACT

Sorption data for H_2O in glassy polyacrylonitrile (PAN) are presented for a range of relative vapor pressures at temperatures from 20°C to 50°C. Simple dual mode sorption, involving "hole-filling" and molecular solution appears to dominate the low activity region of sorption. Based on the clustering analysis suggested by Zimm and Lundberg, pronounced clustering of penetrant appears to occur above a relative pressure of 0.6. The form of the effective concentration-dependent diffusion coefficient for H_2O in PAN, determined by analysis of steady state permeation data, suggests that water in the microvoids and clusters has a lower mobility than the molecularly dissolved water in the polymer matrix. Time lag measurements at high upstream realtive water vapor pressures suggest that the transient state permeation has a non-Fickian character due to relaxations which occur slowly to accommodate the clustering process.

INTRODUCTION

As part of a continuing study of the unique barrier polymer, polyacrylonitrile (PAN) (1), experiments were conducted to characterize the detailed sorption kinetics and equilibria of H_2O in PAN over a range of activities and temperatures. The experiments were guided by the models and analyses frequently used to unify experimental observations of sorption and transport in glassy polymers. The essence of each of the analysis techniques is summarized here to provide a basis for interpretation of the experimental observations.

At low activities, sorption of gases and vapors in glassy polymers is usually described by a superposition of Henry's law and a Langmuir isotherm (2-5). The Henry's law term is generally attributed to molecular solution of penetrants in the glassy matrix. Barrer et al. (5) have suggested that the Langmuir sorption mode occurs as a result of "the insertion of gas molecules into a finite number of pre-existing gaps in the polymer matrix."

At high activities, sorption of vapors in polymers often involves strong positive deviations from Henry's law. Berens (6) has qualitatively described the sorption of vinyl chloride monomer in poly(vinyl chloride) by a "hole-filling" component and a component described by the Flory-Huggins equation. Water sorption isotherms in hydrophobic glassy polymers generally show dramatic upturns at activities above 0.5 to 0.8 (7-9) and the effective diffusion coefficient in such cases often decreases with increasing water concentration (9,10). The combined sorption and transport observations described above are conveniently interpreted in terms of models which invoke "clustering", or non random aggregation of penetrant.

Vieth has discussed a dual mode sorption and transport model for describing cases in which formation of relatively immobile clusters is a dominant feature (11).

Zimm and Lundberg introduced the so-called cluster integral to interpret positive deviations from Henry's law related to the clustering of penetrant in a polymer (12). Williams, Hopfenberg, and Stannett (13) presented a technique for relating explicitly the clustering tendency to the vapor activity dependence of the Flory-Huggins solvent-polymer inter- action parameter, χ. If solvent-solvent contacts are limited to those predicted by the Flory-Huggins random mixing model, the value of χ should be constant over the entire range of activity (13,14). Variation in χ would reflect deviations from simple Flory-Huggins behavior and, therefore, deviations from random mixing.

Barrie et al. (9) have suggested that vapor sorbed at low activities in pre-existing microvoids may serve as nuclei for clusters that presumably persist and grow in cases for which the polymer-penetrant pair are not highly compatible. When the polymer and solute are highly compatible the concentration of penetrant in the matrix at high activities becomes large enough to cause relaxation of the frozen-in pre-existing gaps. This presumably results in "simple" swelling of the essentially homogeneous matrix which can be described in terms of the Flory-Huggins equation for systems such as vinyl chloride monomer in poly(vinyl chloride) (6).

EXPERIMENTAL

A biaxially oriented 0.5 mil polyacrylonitrile (PAN) film provided by the Sohio Company, Cleveland, Ohio, was used in this study. The film

was found to contain trace amounts of a solvent characterized by significant absorption in the infrared spectrum corresponding to amide carbonyl stretching. Essentially all of the solvent was removed by extraction with boiling water as described earlier (1). Standard purification methods were used to prepare high purity samples of H_2O for use in sorption and permeation experiments. Permeabilities and time lags were measured using the modified high vacuum apparatus and techniques described in detail previously (1,15).

RESULTS AND DISCUSSION

Sorption

Sorption isotherms for H_2O in PAN between 20°C and 50°C are presented in Figure 1. The concave downward shape of these isotherms at low pressures manifests dual mode sorption effects resulting presumably from saturation of pre-existing sites in the polymer. Katchman and McLaren (7) have reported data for water in PAN at 25°C. Their data are gratifyingly similar to those presented in Figures 1 and 2. The convergence of the various isotherms of Figure 1 to essentially a single isotherm which adequately represents the normalized results of Figure 2 suggests that the enthalpy of condensation of water is much larger than the enthalpy of mixing associated with the overall sorption process. Berens (6) has reported isotherms for vinyl chloride monomer sorption in poly(vinyl-chloride) similar in general shape to those in Figures 1 and 2. He extended the original dual mode sorption description of the "molecularly

dissolved" mode by replacing Henry's law with the Flory-Huggins equation and referring to the second mode of sorption simply as "hole-filling". Some of the transport results to be presented here for H_2O in PAN suggest that the simple Flory-Huggins form may not be adequate in this system due to marked penetrant clustering.

The technique of Zimm and Lundberg (12) provides a convenient function for evaluating the tendency of a penetrant to cluster in a polymer. Their approach involves analysis of a static sorption isotherm in terms of the so-called cluster integral (G_{11}) defined as:

$$\frac{G_{11}}{V_1} = - \phi_2 \left[\frac{\partial (a_1/\phi_1)}{\partial a_1}\right]_{p,T} - 1 \tag{1}$$

where V_1 is the partial molar volume of the penetrant, a_1 is the penetrant activity and ϕ_1 is the volume fraction of the penetrant. Values of $\frac{G_{11}}{V_1} > -1$ denote a tendency for penetrant to cluster. The quantity $\frac{\phi_1 G_{11}}{V_1}$ measures the average number of penetrant molecules in the neighborhood of a given penetrant molecule in excess of the mean concentration of penetrant in the polymer. This function, therefore, goes to zero in the absence of clustering.

Values of the clustering function, determined from the data in Figures 1 and 2, are presented in Figure 3. The water activity was assumed to be equal to p/p_o and additivity of volumes was assumed in evaluating ϕ_1. The cluster function suggests that significant cluster formation begins at a relative pressure of approximately 0.6.

Transport

The permeability of PAN to water at 30°C as a function of upstream relative pressure is presented in Fig. 4. Although the permeability

varies by only about 6% over the relative pressure range from 0 to 0.4,
the permeabilities at low pressures shown in Figure 4 apparently decrease
slightly with increased pressure consistent with a model which attributes
a lower mobility (relative to the normally dissolved species) to penetrant
sorbed at a finite number of sites in the polymer (16). As the sites
saturate at intermediate concentrations, the effective diffusion coefficient
becomes less influenced by the presence of the sites and the average
mobility rises to the level characteristic of the normally dissolved species.
According to this analysis (often termed "partial immobilization") the net
result of the site saturation with increasing pressure is a permeability
which decreases monotonically with increasing pressure and eventually
reaches an asymptotic limit. The minimum in the permeability suggests that
the partial immobilization model does not adequately describe the results
above a relative pressure of 0.4. Separation of the parameters characterizing
solution and diffusion is useful   to interpret the mechanisms responsible
for the apparent minimum in the plot of permeability versus pressure. An
effective concentration dependent diffusion coefficient, D_{eff}, can be defined
by Eq. (2):

$$N = - D_{eff} \frac{dC}{dx} \tag{2}$$

where N is the flux, C is the concentration of sorbed species and x is the
direction of diffusion. The effective diffusion coefficient can be determined
phenomenologically by graphical differentiation of the permeability, P, and
solubility according to Eq (3) (16).

$$D_{eff} = \left[P(p_2) + p_2 \frac{dP}{dp_2} \right] \left(\frac{dp}{dC} \right)_{p_2} \tag{3}$$

The effective diffusion coefficients defined by Eq. (2) and evaluated by Eq. (3) from the data of Figures 1 and 4 are plotted as a function of C in Fig 5. The low pressure limit of D_{eff} agrees reasonably well with the low pressure limit of the diffusion coefficient determined from the time lag suggesting that, in the low concentration limit, Fickian diffusion applies.

An alternate method of "closing the loop" between the independent sorption, steady-state permeation and transient permeation results is to calculate C/p from Eq. (4), viz:

$$C/p = P/D_a \tag{4}$$

where D_a is the apparent diffusion coefficient determined from a transient permeation measurement of the time lags (θ) shown in Fig.6, D_a is calculated according to Eq. (5):

$$D_a = \ell^2/6\theta \tag{5}$$

where ℓ is the membrane thickness. This technique is rigorously correct only if θ and P are independent of pressure. For relative pressures below 0.4, the error should be small since the variation in P and θ in this regime is rather small and the agreement between the statically measured solubilities (shown by the solid line) and the solubilities calculated from Eq. (4) (shown by the dotted line) in Fig. 7 is quite good. At relative pressures above 0.4, the time lags in Fig. 6 decrease markedly with increasing p/p_0. The time lag cannot decrease for a Fickian system in which the diffusion coefficient decreases with increasing concentration as shown in Fig. 5 . Experimental artifacts related to the use of a finite downstream volume can, of course, cause underestimation of time lags due to an increase in the downstream boundary concentration. This problem

has been discussed by Yasuda and Stannett (15) and Paul (17). In the present study, by reducing the downstream receiving volume by 25%, a reduction of only 5-7% in the measured time lags was observed. The finite size of the downstream volume probably introduces a relatively small error, therefore, in the calculated transport coefficients. It is however, possible that truly non-Fickian processes contribute to the deviations observed. Non-Fickian behavior can occur when the diffusion coefficient tends to decrease with time and the solubility coefficient increases with time due to slow molecular relaxations (18). Clustering does not necessarily imply non-Fickian behavior. Non-Fickian anomalies occur when molecular relaxations, required to accommodate such clustering, proceed in the same time scale as diffusion. Barrie and Machin (19) observed that the diffusion coefficient of H_2O in poly(propyl-methacrylate) decreased with increasing concentration. They suggested that clustering was responsible for the observed decrease. Diffusion coefficients calculated from their transient and steady-state data were mutually consistent, indicating that the transport behavior was Fickian over the entire range of experimental conditions.

The functional form of D_{eff} in Fig. 5 provides evidence that water clustering is indeed occuring at high activities. The decrease in the effective diffusion coefficient at high water concentrations is, in fact, typical of clustering and has been discussed in detail elsewhere (20,21). Both the sorption data in Fig. 1 and the steady-state transport data are, therefore, consistent with the development of relatively immobile clusters at high water activities.

Barrie and Platt (9) suggest that water sorbed in pre-existing "gaps" at low activities may serve as nuclei for cluster formation at high activities. This seems consistent with the composite behavior described by the results of Fig. 5. Specifically, the effective diffusion coefficient in typical dual mode systems at low activities increases with concentration as the ratio of the concentration of more mobile (dissolved) species to less mobile (Langmuirian) species increases. If, however, at some critical concentration, the fraction of molecules in the low mobility mode is increased (over and above the Langmuir saturation capacity due to cluster growth) then the effective diffusion coefficient should go through a maximum with continued increases in concentration, consistent with the experimental observations presented in Fig. 5. Presumably, for systems which do not exhibit clustering at high activities, the Flory-Huggins description of the chemical potential provides an adequate representation of the sorption behavior and the effective diffusion coefficient defined in Eq. (2) would increase monotonically with concentration as the matrix becomes swollen. Barrie et al. (22,23) have also reported clustering of water in several rubbers, so the existence of frozen pre-existing gaps in the polymer must not be a necessary criterion for clustering, since these gaps do not exist in the rubbery state.

CONCLUSIONS

The concept of two modes of sorption is useful for interpreting transport phenomena of water vapor at both low and high relative pressures in glassy polyacrylonitrile. At intermediate values of p/p_0, clustering becomes apparent and, therefore confounds the relatively simple dual mode model.

Both the clustered and unclustered species in the "second mode" seem to have significantly lower mobility than the molecularly dissolved species. The pre-existing microvoids may, therefore, be precursors for clustering developed at high activities.

Non-Fickian aspects of transport are suggested by the time lags which decreased with increasing relative pressure although the diffusion coefficient, calculated from steady-state experiments, decreases with increasing concentration at activities corresponding to incipient clustering. This non-Fickian behavior can be interpreted in terms of a diffusion coefficient which tends to decrease and a solubility coefficient which tends to increase with time due to relaxations in the polymer which may be required to accommodate the clustering process.

ACKNOWLEDGEMENTS

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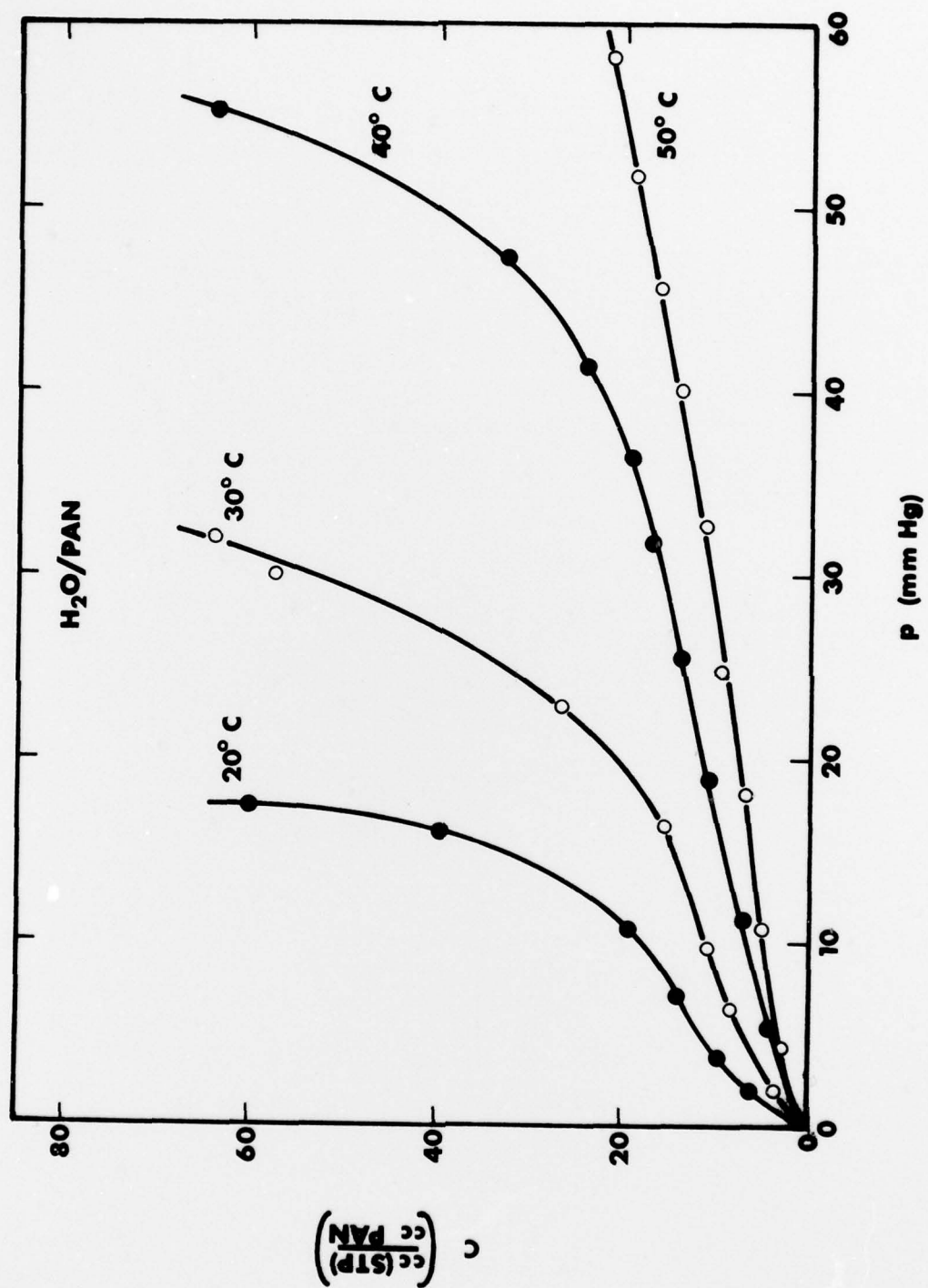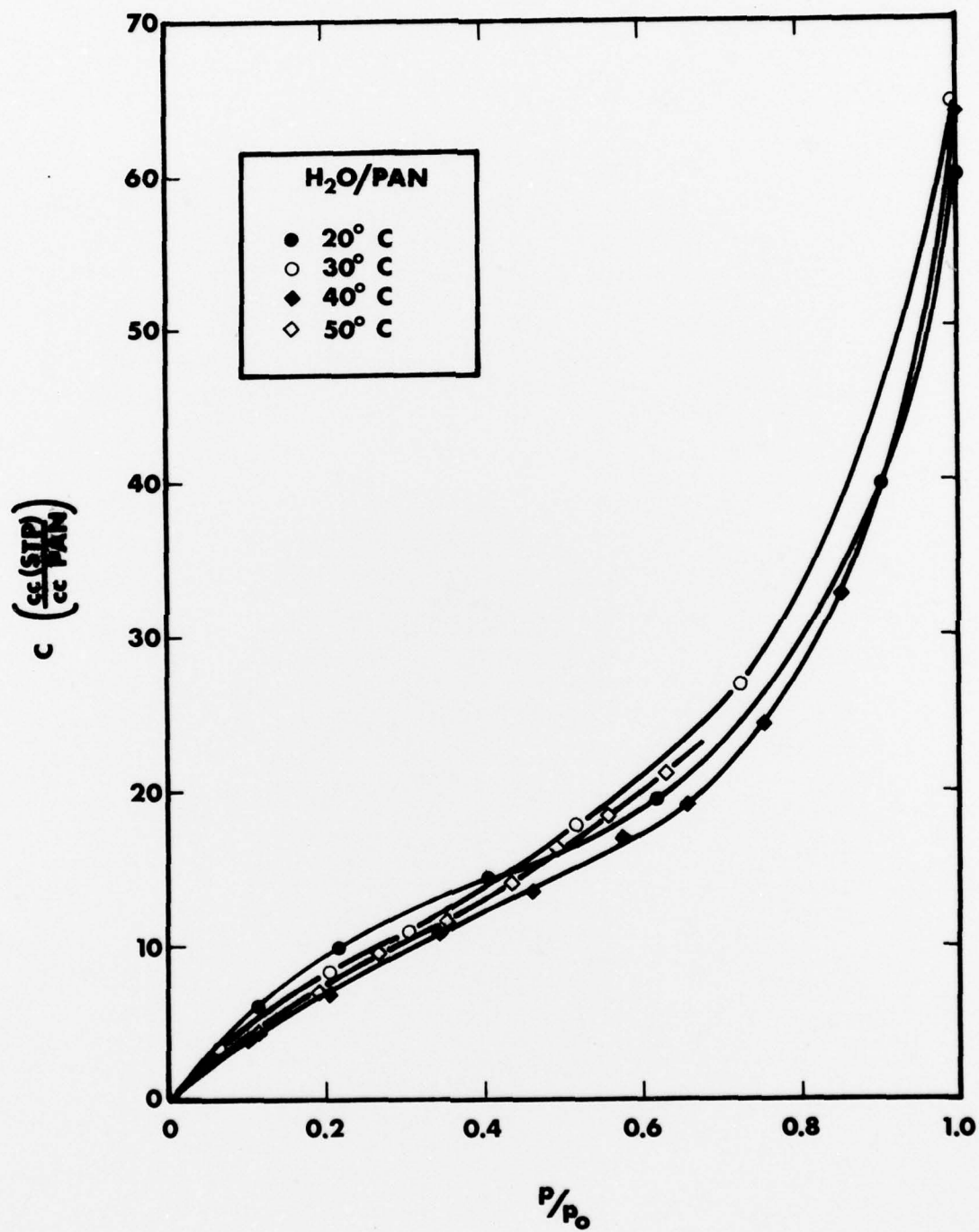23. J. A. Barrie and D. Machin, J. Macromol. Sci., Phys. B3, 645 (1969).
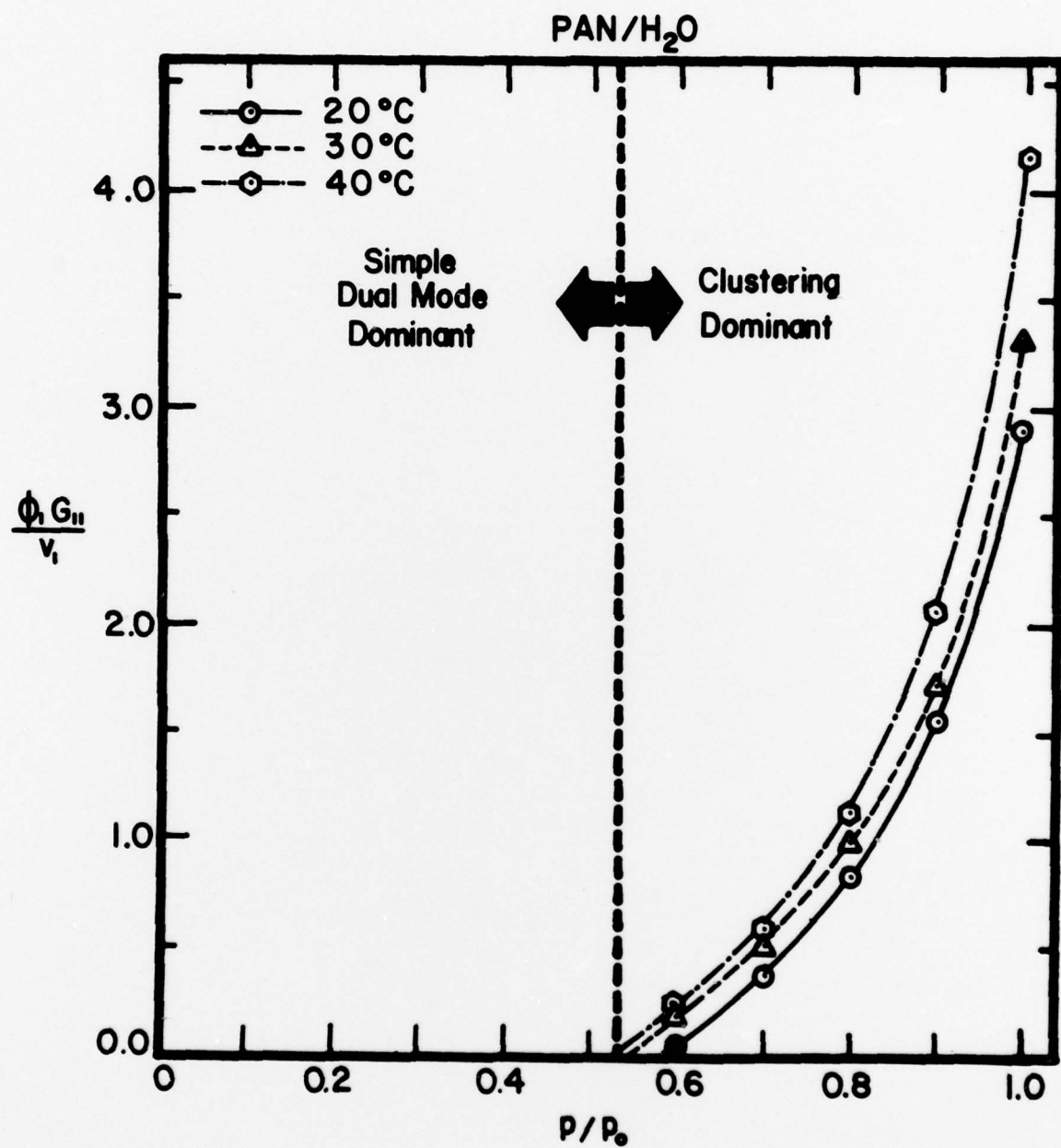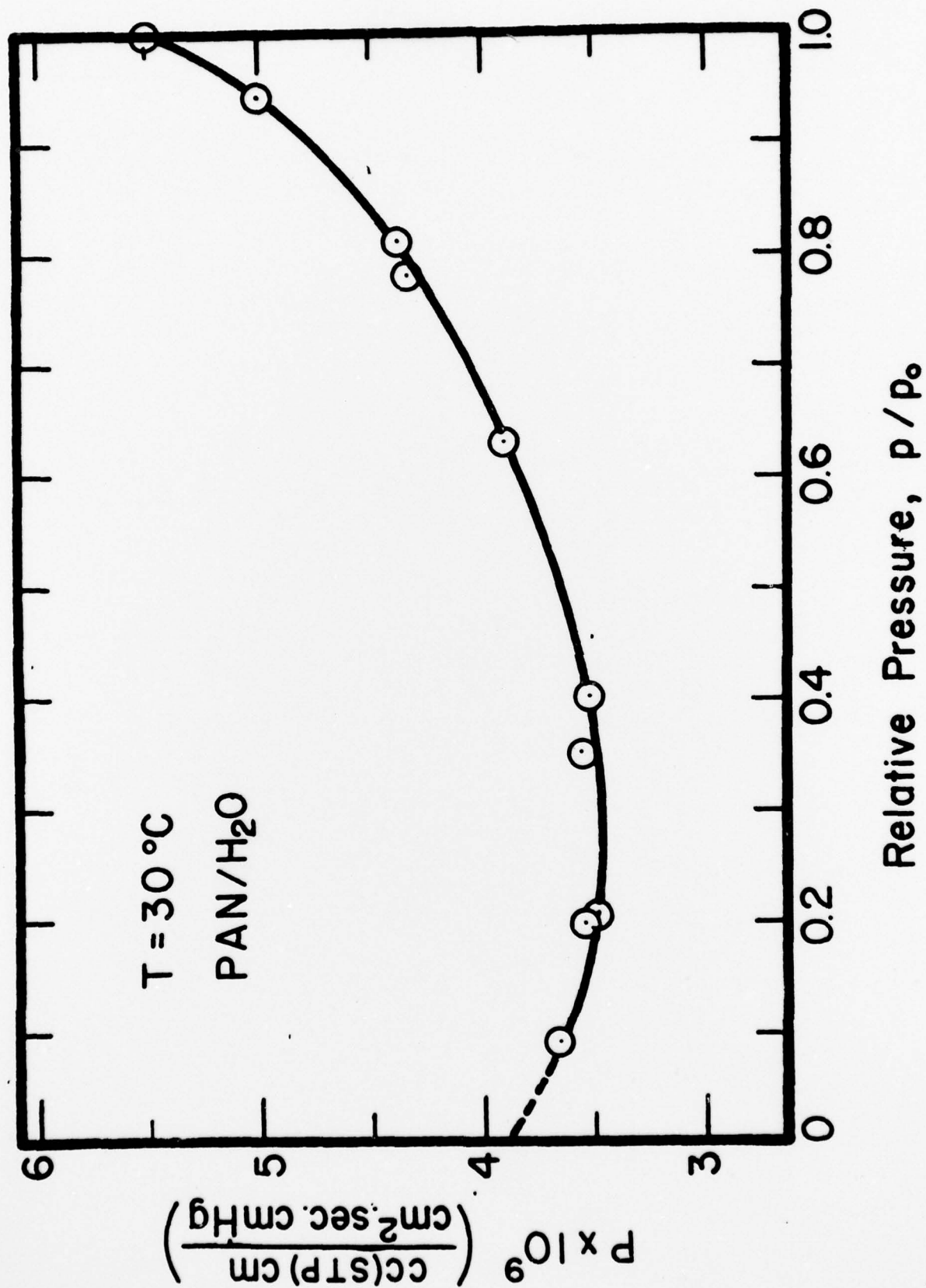
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LIST OF FIGURE CAPTIONS

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 7

T = 30°C
● H₂O / PAN (QZ Spring)
⊙ H₂O / PAN (from Transport, P×p/D₂)